

Photoacoustic study of airborne and model aerosols

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(Presented on 25 June 2002)

Airborne particulates of either natural or anthropogenic origin constitute a significant portion of atmospheric pollution. Environmental xenobiotics, among which are polynuclear aromatic hydrocarbons (PAHs) and pesticides, often adsorb to aerosols and as such are transported through the atmosphere with the physicochemical properties of the aerosols determining the lifetime of these organic compounds. As an example, the resistance of some PAHs against the photolysis is explained by the effect of the aerosol's "inner filter" that reduces the intensity of incident light reaching the mineral particles. On the other hand, some constituents of the aerosols can act as catalytic and/or stoichiometric reagents in atmospheric reactions on the solid surfaces. In the study described here the photoacoustic (PA) spectroscopy in the UV-Vis was used to investigate natural and model aerosols. The PA spectra obtained from coal and wood ashes and of Saharan sand, all three representatives of airborne aerosols, provide the evidence for the existence of the "inner filter." Furthermore, valuable information about the different nature of the interaction between the model aerosols and adsorbed organics (e.g., PAH-pyranthrene and silica, alumina, and MgO) has been obtained. Finally, the outcome of the study conducted with powdered mixtures of chalk and black carbon suggests that the PA method is a candidate method for determination of carbon content in stack ashes. © 2003 American Institute of Physics. [DOI: 10.1063/1.1512769]

I. INTRODUCTION

Airborne particulates represent a significant portion of atmospheric pollution of either natural (sea spray, desert sand, volcano ashes) or anthropogenic origin (fuel combustion ashes). Various physicochemical properties of aerosols are responsible for reduced visibility but also for chemical reactions of some pollutants in the atmosphere. For example, reflectance (specular and diffuse) and absorbency are inversely proportional to particle size; the absorbency also depends on the chemical composition.

Environmental xenobiotics like polynuclear aromatic hydrocarbons (PAHs) and/or pesticides are often adsorbed to aerosols of various chemical composition and as such are transported in the atmosphere. Numerous laboratory experiments have been performed in an attempt to predict behavior of pollutants and their lifetimes in the real atmosphere. The results of the studies suggest that some solid model carriers e.g., silica, could catalyze chemical degradation of PAHs and pesticides,^{1,2} while others (such as fly ashes) act as stoichiometric oxidants in chlorination of aromates.³ Furthermore, photodecomposition experiments in simulated atmospheres

have shown that pesticides adsorbed on kaolin, a terrogenic aerosol, can travel over long distances, while those adsorbed on a fly ash (an urban aerosol) photodegrade rapidly. It is the presence of metal and metal oxides in the fly ash that is responsible for such rapid degradation.⁴ Earlier studies have also demonstrated stability against photolysis of PAHs (e.g., pyrene) when adsorbed on fly ash surfaces.⁵ Results of additional investigations showed that pyrene is particularly well stabilized on carbonaceous, and to a lesser extent on magnetic subfraction of the coal fly ash, while the mineral subfraction (the major component) exhibits a high photoreactivity.⁶ Besides a varying affinity of pyrene to adsorb to various subfractions, the stabilizing effect of coal ash may be due to the "inner filter" effect of the magnetic subfraction (with a lowest affinity to pyrene) that absorbs much of the incoming light, decreasing thereby the intensity of light incident upon mineral particles and hence affecting the photoreactivity.⁶

The PA method was used here to investigate the physical-chemical properties of some model and airborne aerosols. Additionally, an attempt was also made to use the same technique for qualitative determination of elemental carbon in powdered samples, such as various fly ashes.

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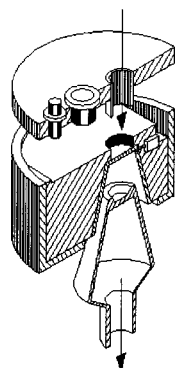


FIG. 1. The homemade PA cell suitable for studies on powdered samples.

II. EXPERIMENT

A. Samples

In order to coat the carrier, the powders were immersed in a toluene solution of pyranthrene and a rotary evaporator was used to slowly evaporate the solvent. The amount of coated compound was quantitatively determined spectrophotometrically subsequent to eluting in toluene the organics from the powdered sample (20–40 mg).¹

B. Equipment

Two different experimental setups have been used. In the first study the objective of which was to investigate adsorbant–adsorbate interactions, the apparatus consisted of a 450 W high pressure xenon arc lamp (XBO 450 Osram), a 25 cm Czerny–Turner monochromator (PTI), a mechanical chopper (HMS 222) operating at 63 Hz, and a PA cell (MTEC/100). The signal from the condenser microphone (Bruel&Kjaer) was filtered using a Butterworth filter (4302 Dual 24 db/Octave Filter, Ithaco) and then detected by a lock-in amplifier (Ithaco 399). Data acquisition and instrument control were performed by an IBM-AT compatible computer (Hewlett-Packard).

In the second experiment designed to acquire PA spectra of different aerosols, the setup consisted of a Xe lamp (Osram XBO-450 watt), a dual grating monochromator (SpectraPro-150, Acton Research) with 20 nm resolution, a mechanical chopper (EGG model 165), and a homemade PA cell was used. After leaving the monochromator, the colli-

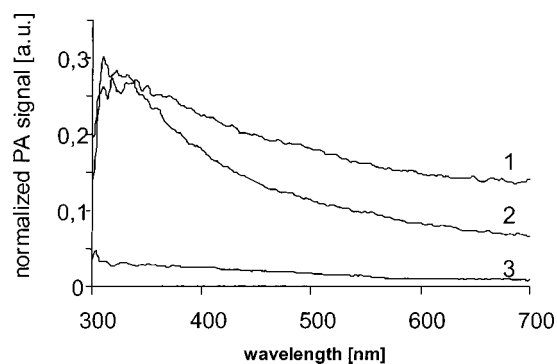


FIG. 2. The PA spectra of the airborne aerosols: (1) coal ash, (2) wood ash, and (3) Saharan sand.

ated radiation was mechanically chopped (30 Hz), collected by a quartz lens, and focused into the PA cell using a parabolic mirror.

The PA cell (Fig. 1) was made from a pair of polished standard glass taper joints that when assembled together ensure a very good degree of acoustic insulation from the external noise sources.^{7,8} The radiation enters the PA cell through a quartz window mounted at the top. The 3 mm long capillary (diameter 300 μm) was used to achieve coupling between the sampling volume and the M32 (Microtel) miniature microphone. The output signal from the microphone was detected at the modulation frequency using a lock-in amplifier (SR830) before being processed by the computer.

III. RESULTS AND DISCUSSION

The PA spectra of coal and wood ashes, and of Saharan sand, all three being the representatives of airborne aerosols, are shown in Fig. 2. The results support the evidence for the existence of the “inner filter” that is crucial for the stability of some PAHs against the photolysis. Samples of coal ash exhibit the highest absorbency in the UV-Vis range presumably due to the highest content of carbon and iron oxide among the aerosols studied.^{9,10} On the other hand Saharan sand with the lowest content of carbon and iron oxide also showed the lowest absorbency.

Another likely reason for the stabilizing effect observed in the adsorbed state is a different nature of the interaction between the adsorbent and adsorbate. As in the case of clay–mineral and organics interactions, the operating forces range from a dipole–dipole attraction to a pure coordinative covalent bonding, including the important roles of hydrogen bonding and interactions.¹¹

Early studies of interaction between PAH and the adsorbent provide the evidence for a redshift in the absorption spectrum of $\pi \rightarrow \pi^*$ transitions whenever PAHs adsorb to a relatively polar surface, such as silica-gel.^{12,13} In the case of a pure physical adsorption, the spectrum of the adsorbed molecule is very similar to that of the free molecule.¹⁴ Detailed investigation of the photophysics of pyrene adsorbed on silica-gel, alumina, and CaF_2 solid carriers showed the strongest interaction between this PAH and alumina. In the case of CaF_2 the adsorption of pyrene is purely physical.¹⁵ The strongest interaction between PAH and alumina is attributed to a more complex electronic state arising from the adsorption with the generated cation having no possibility for a spin motion. The reason for this is that molecular orbitals (MO) of cation and the atomic orbitals (AO) of oxygen atoms at the surface of alumina overlap more strongly forming an extended MO.¹⁶

The PA spectra of pyranthrene (a high molecular weight PAH) adsorbed on MgO ($d \approx 1 \mu\text{m}$), alumina ($d = 20 \text{ nm}$), and silica-gel ($d = 3\text{--}6 \text{ nm}$) and the UV-Vis spectrum of its toluene solution are given in Fig. 3. The PA spectrum most resembling that of the toluene solution of pyranthrene was obtained when MgO was used as a solid carrier. Compared to the absorption spectrum of toluene solution, the entire PA spectrum appears blueshifted, as it can be expected when coating the organic compound on a solid carrier.¹³ Thus the

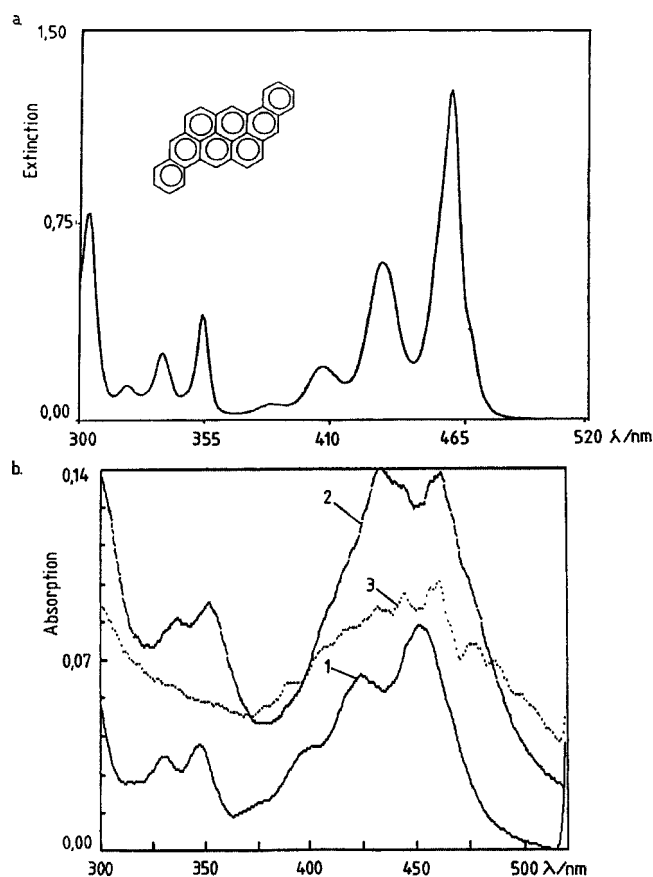


FIG. 3. Pyranthrene: (a) UV-Vis spectrum in toluene and (b) PA spectra of MgO (1), alumina (2), and silica-gel (3).

maximum (at 462 nm) observed in toluene solution is shifted to 450 nm when pyranthrene was coated on MgO. The ratios of peak intensities in the PA spectra of the coated and ground samples are practically equal indicating no interaction with the adsorbent¹³ (i.e., the compound is only physically adsorbed). The PA spectrum of pyranthrene coated on alumina shows a somewhat different structure. Instead of three there are only two peaks in the Vis region (at 432 and 461 nm) of almost equal magnitudes. The minor redshift observed for the strongest band (as already observed with PAHs coated on alumina¹⁷), as well as the change in the peak intensity ratio, could be indicative for a stronger substrate-PAH interaction. The evidence for unchanged structure in the UV region might be in favor of the assumed interaction. When pyranthrene is adsorbed on the silica-gel the shape of the PA spectrum changes completely. In the visible region the spectrum exhibits more structure than that of toluene solution of the same compound and of pyranthrene coated on MgO. On the other hand, the UV region showed no resolved structure possibly indicating some photodecomposition on the silica-gel surface as well.¹⁵

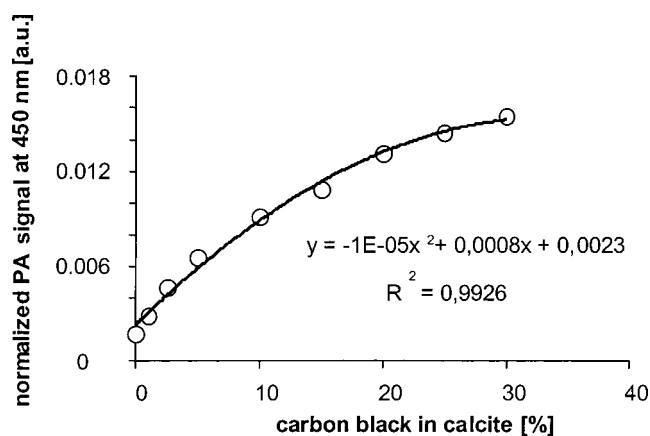


FIG. 4. The PA signal at 450 nm (normalized to that of carbon black) for calcite doped with a different percentage of carbon black.

Since the PA spectrum is usually normalized against that of a perfect absorber such as carbon black, the idea was born that PA spectroscopy might prove to be a valuable tool when determining the carbon content in powdered samples such as, for example, various stack ashes. Therefore mixtures of calcium carbonate (chalk) with a different percentage of carbon black were prepared and their PA signals recorded at 450 nm. The calibration curve (Fig. 4) shows a quadratic dependence of the signal on the percentage of carbon.

Overall, the outcome of the study indicates the feasibility of the PA spectroscopy in detecting physical-chemical properties of natural and model aerosols.

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